Recovery process of degraded ferroelectric properties in the forming-gas-annealed Pt/Bi 4−x La x Ti 3 O 12 / Pt capacitor

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Citation: Applied Physics Letters **82**, 1577 (2003); doi: 10.1063/1.1558970
View online: http://dx.doi.org/10.1063/1.1558970
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/82/10?ver=pdfcov
Published by the AIP Publishing

Recovery process of degraded ferroelectric properties in the forming-gas-annealed Pt/$Bi_{4-x}La_xTi_3O_{12}$/Pt capacitor

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(Received 17 October 2002; accepted 11 January 2003)

The recovery of ferroelectric properties in the forming-gas-annealed Pt/$Bi_{4-x}La_xTi_3O_{12}$/Pt (Pt/BLT/Pt) capacitor was studied by examining changes in ferroelectric responses, phase evolution, and spatial distributions of relevant species during the recovery annealing. The degraded ferroelectric properties were practically restored to their original values after the recovery annealing at 600 °C for 10 min in an O_2 atmosphere. The following recovery process has been delineated from the present study: (i) the removal of impregnated protons from the degraded capacitor due to the chemical potential difference of protons between the forming-gas-annealed capacitor and the contacting atmosphere, and (ii) the restoration of perovskite BLT phase with the help of replenishment of the Bi and oxygen losses via diffusion from the neighboring intact region to the Bi-depleted columnar region located beneath the top Pt electrode.
[DOI: 10.1063/1.1558970]

The $Bi_{4-x}La_xTi_3O_{12}$/Pt (BLT/Pt) capacitor[1,2] has been of particular interest because of its fatigue-free characteristics coupled with relatively large remanent polarizations as compared to those of fatigue-free $SrBi_2Ta_2O_9$ (SBT)-based capacitors.[3] Despite these promising features for nonvolatile ferroelectric random access memories (FRAM), like other important ferroelectric capacitors such as Pt/SBT/Pt[4–6] and Pt/Pb(Zr,Ti)O_3(PZT)/Pt,[7,8] the Pt/BLT/Pt[9,10] capacitor seriously degrades its ferroelectric properties during the forming-gas-annealing (FGA) step. Thus, one of the most important remaining subjects in the practical implementation of the BLT capacitor to high-density FRAM is to establish a convenient recovery method of the degraded capacitor.[11]

According to a previous study,[9] the degradation mechanism of the Pt/BLT/Pt ferroelectric capacitor during FGA can be summarized as: (i) the catalytic dissociation of H_2 to produce protons and electrons by the top Pt electrode, (ii) the columnar penetration of protons into the BLT layer, and (iii) the decomposition of perovskite BLT phase into $(Bi,La)_2Ti_2O_7$ and Ti_6O_{11} phases by the following equation:

$$\begin{aligned}&6Bi_{4-x}La_xTi_3O_{12}(BLT)+38H^{+}+38e'\\&\quad\leftrightarrow 6(Bi_{2-x}La_x)Ti_2O_7+Ti_6O_{11}\\&\quad+12Bi(g)+19H_2O(g).\end{aligned} \tag{1}$$

In view of Eq. (1), the main purpose of this study is to elucidate the recovery mechanism, particularly paying attention to the removal of impregnated protons from the columnar region and the restoration of the decomposed BLT phase.

Highly c-axis oriented $Bi_{4-x}La_xTi_3O_{12}$ (BLT) films were prepared on Pt/TiO_2/SiO_2/Si substrates using metalorganic sol decomposition. Following the previous study,[9] we employed $x=0.85$ for the composition of BLT films. Details of the sol preparation and coating process are described elsewhere.[12] The film thickness, as determined using a field-emission scanning electron microscope, was 280 nm. The BLT-based capacitors with top Pt electrodes covering the whole surface area of the film were fabricated. These are called ''sandwich'' capacitors. In addition to these, the BLT capacitors having top Pt electrodes with the diameter of 600 μm were also prepared (dot capacitors). The FGA-treated Pt/BLT/Pt capacitors were prepared by annealing the capacitors at 400 °C for 10 min in an atmosphere of 4% H_2-N_2 mixture. The degraded capacitors were then annealed at various temperatures between 400 and 900 °C for 10 min either in an O_2 or in a N_2 atmosphere to examine the recovery process. Measurements of ferroelectric properties were performed using an RT6000S ferroelectric tester.

Figure 1 presents polarization–voltage ($P-V$) hysteresis loops of the Pt/BLT/Pt capacitors before and after FGA as well as those of the FGA-treated capacitors after the recovery annealing at three indicated temperatures for 10 min. The Pt/BLT/Pt capacitor before FGA shows a well-saturated $P-V$ hysteresis loop. In contrast to this, the FGA-treated capacitor exhibits a characteristic shape of a leaky loop. Figure 1 shows that the FGA-treated capacitor retains its leaky shape even after the recovery annealing at temperatures up to 500 °C in an O_2 atmosphere. The leaky loop becomes a typical ferroelectric $P-V$ hysteresis loop only after the recovery annealing at 600 °C for 10 min in an O_2 or in a N_2 atmosphere. The electrical polarization values ($2P_r$) of the recovery-annealed capacitors were 34 μC/cm^2 for O_2 annealing and 23 μC/cm^2 for N_2 annealing. The recovery rates were 94% and 64%, respectively, of the original $2P_r$ value before FGA. The results indicate that the recovery rate of the

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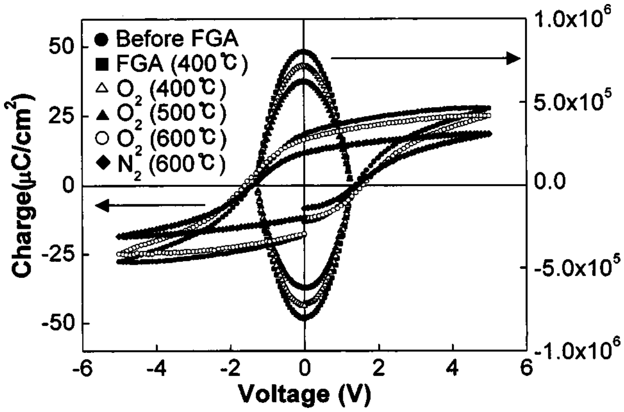

FIG. 1. Polarization–voltage ($P-V$) hysteresis loops of the Pt/BLT/Pt dot capacitors before and after FGA (4% H_2-N_2 mixture gas) at 400 °C for 10 min and of the FGA-treated capacitors after the recovery annealing at three indicated temperatures for 10 min.

FGA-treated Pt/BLT/Pt capacitor is strongly influenced by the annealing atmosphere. Contrary to this, it was reported that ferroelectric properties of the FGA-treated PZT-based capacitor were fully recovered by thermal annealing in a N_2 atmosphere.[7] This suggests that the recovery mechanism of FGA-treated capacitors depends on the nature of ferroelectric materials involved.

Having identified the role of the recovery annealing in the restoration of ferroelectric properties, we now examine the effect of the recovery annealing on the restoration of the perovskite BLT phase. The decomposition of BLT during FGA is induced by the penetrating protons, as outlined in Eq. (1). It was further shown that the impregnated protons existed only in the columnar region.[9] Thus, it is highly probable that the decomposition is spatially limited to the protons-impregnated columnar region just beneath the top Pt electrode. To examine the role of the protons-impregnated columnar region in the FGA step and in the recovery process, we have employed a synchrotron x-ray beam (8C1 POSCO beam line of the Pohang Light Source) which is capable of focusing on a small area of (400×400) μm^2 and of detecting a weak x-ray microdiffraction (XRMD) signal.

Figure 2(a) presents XRMD patterns of the FGA-treated Pt/BLT/Pt sandwich capacitors after the recovery annealing at five indicated temperatures in an O_2 atmosphere for 10 min. As indicated in the bottom pattern, the decomposition of BLT in the FGA-treated sandwich capacitor leads to the formation of $(Bi,La)_2Ti_2O_7$ and Ti_6O_{11}.[9] The restoration of the BLT phase commences only after the recovery annealing at a temperature above 700 °C. Figure 2(b) presents XRMD patterns of the FGA-treated dot capacitors after the recovery annealing under various conditions and compares these with the pattern of a fresh dot capacitor before FGA. In contrast to the sandwich capacitor, the FGA-treated dot capacitor (second pattern from the bottom) does not show any pattern associated with the formation of $(Bi,La)_2Ti_2O_7$ and Ti_6O_{11} but shows the peaks corresponding to the BLT $(00l)$ reflections, in spite of a substantial reduction in their intensities. This suggests a partial decomposition of the BLT phase during the FGA step at 400 °C. The XRMD intensity increases gradually with increasing annealing temperature. The intensity corresponding to the BLT $(00l)$ reflections recovers 90% of

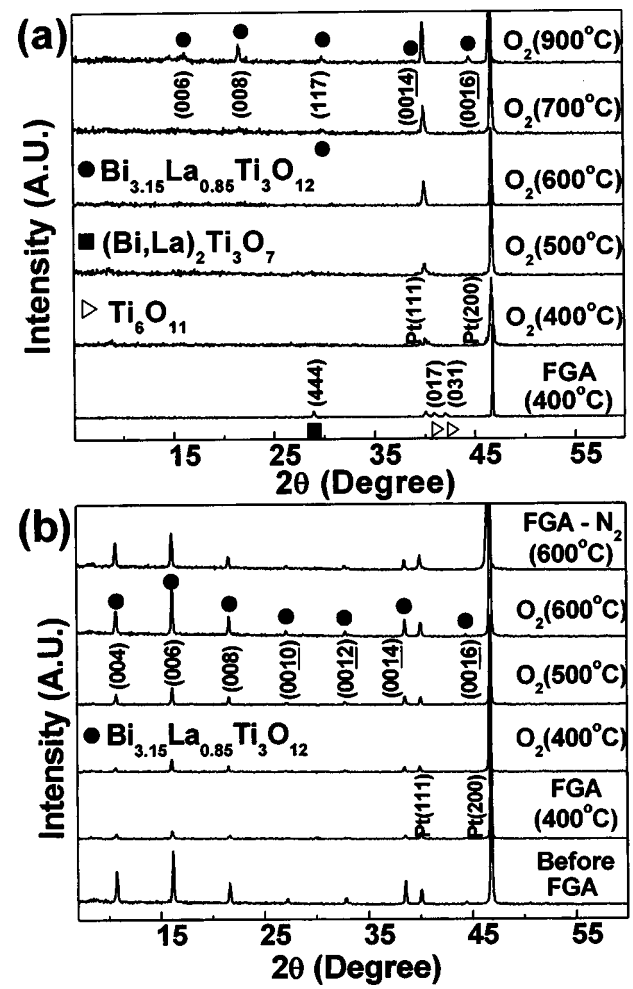

FIG. 2. XRMD patterns (400×400 μm^2) of two different types of Pt/BLT/Pt capacitors thermally treated under various conditions: (a) XRMD patterns of the FGA-treated sandwich capacitors after the recovery annealing at five indicated temperatures in an O_2 atmosphere for 10 min, and (b) XRMD patterns of as-prepared fresh capacitor before FGA and of the FGA-treated dot capacitors (from the columnar region) after the recovery annealing either in an O_2 or in a N_2 atmosphere at an indicated temperature for 10 min.

its original value (before FGA) after the recovery annealing at 600 °C for 10 min in an O_2 atmosphere.

We now examine the changes in spatial distributions of relevant species in the FGA-treated dot capacitor after the recovery annealing with the help of a three-dimensional mapping technique using a secondary ion mass spectrometer (SIMS) equipped with a sputtering apparatus. The impregnated protons in the FGA-treated capacitor gradually disappeared with increasing annealing temperature. As illustrated in Fig. 3(a), the protons were completely removed after the recovery annealing at 600 °C for 10 min in an O_2 atmosphere. This clearly supports our previous assertion that the recovery of ferroelectric responses after the annealing at 600 °C (Fig. 1) is a consequence of the removal of residual protons. Figures 3(b) and 3(c) indicate that the Bi and oxygen losses in the FGA-treated capacitor occur mainly at the columnar region beneath the top Pt electrode. This observation is consistent with the prediction of Eq. (1) and explains the decrease in the XRMD intensity of BLT $(00l)$-type reflections in the FGA-treated dot capacitor [Fig. 2(b)]. The SIMS images show that the Bi and oxygen losses are prac-

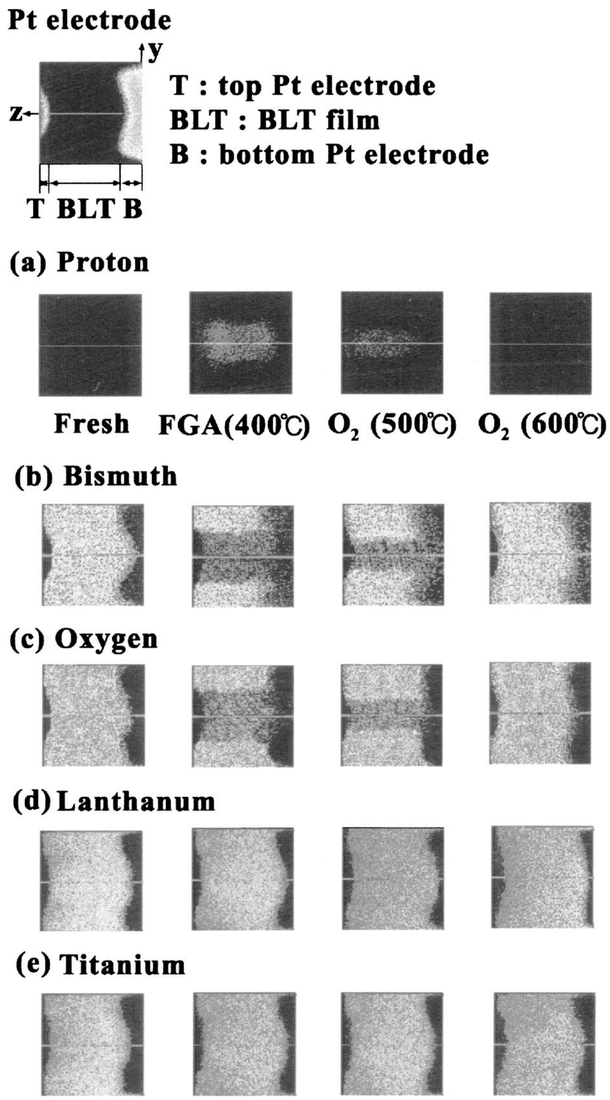

FIG. 3. SIMS images of protons, bismuth, oxygen, lanthanum, and titanium ions along the direction normal to the surface of capacitors, showing that the spatial distributions of protons, bismuth, and oxygen in the Pt/BLT/Pt capacitor are greatly influenced both by FGA and by the recovery annealing. The area employed in the SIMS mapping was $(300\times300)\ \mu m^2$.

tically retrieved by the recovery annealing at 600 °C, supporting the observed restoration of the BLT phase under the same annealing conditions [Fig. 2(b)]. Contrary to proton, bismuth, and oxygen, the spatial distributions of lanthanum and titanium were little affected by the FGA step and by the recovery annealing, as shown in Fig. 3.

According to Eq. (1) and the mapping result given in Fig. 3, the evaporation loss of Bi and oxygen in the dot capacitor mainly comes from the columnar region containing the impregnated protons.[9] Because of the columnar nature of proton penetration, the dot capacitor possesses the intact bare BLT region having relatively higher contents of Bi and oxygen but with a negligible concentration of protons (Fig. 3). Consequently, the Bi and oxygen losses in the columnar region during FGA can be compensated by a simultaneous replenishment of Bi and oxygen via diffusion from the neighboring bare BLT region. The replenishment of the Bi loss during the recovery annealing was also observed in the FGA-treated Pt/SBT/Pt dot capacitor though the analysis was limited to the surface region (~50 Å).[4] This complement inhibits a complete decomposition of the BLT phase during FGA [Fig. 2(b)]. On the other hand, the observed enhanced restoration of BLT by O_2 annealing, as compared to N_2 annealing at 600 °C, can be attributed to the improved replenishment of oxygen loss from oxygen ambience. This also explains the observed difference in the recovered $2P_r$ value between the O_2-annealed BLT capacitor and the N_2-annealed capacitor (Fig. 1). The partial recovery of degraded ferroelectric properties after the O_2 annealing was also observed in the FGA-treated SBT capacitor.[7] In this case, however, no study was reported on the degree of recovery after the N_2 annealing.

In contrast to the dot capacitor, the sandwich film capacitor does not have a bare region because the whole surface is covered with the top Pt electrode. In this case, the decomposition of BLT into $(Bi,La)_2Ti_2O_7$ and Ti_6O_{11} would be expedited during FGA because of the absence of the simultaneous replenishment of Bi and oxygen from the nearby intact BLT region. In addition to this, as shown in Fig. 2(a), the restoration of BLT according to Eq. (1) would be suppressed because the complement of the Bi loss is not expected. Thus, one can explain the accelerated decomposition of the BLT phase during FGA as well as the retarded restoration during the recovery annealing observed in the sandwich capacitor, as compared with those in the dot capacitor.

In conclusion, the recovery of degraded ferroelectric properties in the FGA-treated Pt/BLT/Pt capacitor was achieved by both the removal of impregnated protons and by the restoration of ferroelectric BLT phase with the help of replenishment of the Bi and oxygen losses via diffusion from the neighboring intact region. Contrary to proton, bismuth, and oxygen, the spatial distributions of lanthanum and titanium were little affected by the FGA step and by the recovery annealing.

This work was supported by the KISTEP of Korea through the NRL Program.

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